

Freezing Point Depression to Determine Molar Mass

Introduction

The nominal definition of a solution is a mixture of two components; one is present in a greater quantity over the other. The term solvent refers to the component in larger quantity and the term solute refers to the component in smaller quantity. These definitions apply to solutions in the solid, liquid, or gaseous phase. There are four different commonly used terms that express the relative amount of solute to solvent. For solid solutions, the mass percent is commonly used for quantity. The mole fraction is used to describe the relative amount of solutes in gaseous solutions, and molarity for liquid solutions. The definition of each is given below:

$$\text{Mass Percent} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

$$\text{Mole Fraction} = X = \frac{n_1}{n_1 + n_2}$$

$$\text{Molarity} = M = \frac{\text{moles of solute}}{L \text{ of solvent}}$$

$$\text{Molality} = m = \frac{\text{mole of solute}}{\text{kg of solvent}}$$

For measurement involving phase changes (i.e. melting), molarity (M) is not used since the volume of solution changes dramatically from one phase to the other. Rather molality (m) is used since this quantity is independent of the volume of the solution.

Why Does Salt Melt Ice?

At one atmosphere of pressure, ice melts at exactly 0°C. Solid water and liquid water are in equilibrium with each other—the rate of freezing and melting are equal. Once a solute or “foreign particles” are added, the equilibrium is disrupted. The foreign molecules dissolve in the water, but do not pack easily into the array of molecules in the solid. The total number of liquid water molecules captured by the ice per second goes down, so the rate of freezing goes down. The rate of melting is unchanged by the presence of the foreign material so melting occurs faster than freezing. This is why aqueous solutions melt at lower temperatures than pure ice does.

This phenomenon has practical uses as well as scientific uses. Practical uses include using salt to lower the temperature of water freezing on roads and planes, etc. Scientists use the freezing point depression to calculate the molecular weight of unknown compounds. The

freezing point depression, ΔT , between the melting temperature of pure solvent and that of a solution of solvent and solute molecules is given by:

$$\Delta T = T_{\text{pure solvent}} - T_{\text{solution}}$$

The freezing point depression for a nonelectrolyte solution is given by:

$$\Delta T = K_f m_{\text{solute}}$$

ΔT has the units of $^{\circ}\text{C}$, or K, m is the moles of solute/kg of solvent, and K_f is the freezing point depression constant which varies with solvent. The table below gives the freezing point depression constants for several solvents:

Solvent	Freezing Point ($^{\circ}\text{C}$)	K_f ($^{\circ}\text{C}/m$)
Carbon tetrachloride	-22.8	29.80
Water	0.0	1.86
Benzene	5.5	2.53
Cyclohexane	6.5	20.10
Phenol	43.0	7.27
Lauric acid	44.0	3.90
Camphor	179.0	39.70

Molality is used for the concentration term instead of molarity because the latter changes as the volume expands and contracts. When the solute dissociates, more particles are introduced into the solution. A correction factor known as the van't Hoff correction factor is used to account for dissociation of the solute. The freezing point depression equation becomes:

$$\Delta T = i K_f m$$

i is the van't Hoff correction factor and ideally equals the number of ions in solution. Sodium chloride, NaCl, for example, would have a correction factor of two because it dissociates into two ions, Na^+ and Cl^- . If the concentration of the solute is high, then the “disrupting particles” (ions) are not all acting independently and the van't Hoff correction factor (i) would be less than two for NaCl.

In this experiment, the freezing temperature of the pure solvent, lauric acid, $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$ is found first. Then the freezing point of a solution prepared from a mixture of an unknown organic acid and lauric acid will be measured. By measuring the freezing point depression and knowing the masses of the unknown organic acid and lauric acid in the mixture the molecular weight of the unknown acid can be found. Then you will investigate what happens when a dissociating solute is added to water.

Prelab Questions

- 1) Which of the following aqueous solutions would have the lowest freezing point temperature: 0.050 m CaCl_2 or 0.10 m HCl ? Justify your answer.
- 2) Why is the freezing point of pure lauric acid determined experimentally instead of just assuming that it is 0°C ?
- 3) What is the ideal van't Hoff correction factor for MgCl_2 ?

Procedure

Determination of Freezing Point of Lauric Acid

- 1) Set up a ring stand with a test tube clamp next to a hotplate.
- 2) Obtain a 400 or 600 mL beaker and fill about $\frac{3}{4}$ full with water. Place the beaker on the hotplate and begin to heat it.
- 3) Weigh out approximately 8 grams of lauric acid into a weighed test tube. Record the exact mass.
- 4) Place the test tube into the test tube clamp and lower into the hot water bath. Heat the acid until it is liquefies (about $60\text{-}80^\circ\text{C}$). Use a thermometer to stir the acid.
- 5) As the lauric acid is heated, obtain another 400 or 600 mL beaker and fill with about 350 mL of tap water.
- 6) As soon as the lauric acid is liquid, quickly transfer the test tube into the second beaker and immediately begin recording the temperature.
- 7) Record the temperature every 30 seconds for 10 minutes. Stir the lauric acid with the thermometer on a regular basis, until the acid begins to solidify.
- 8) Once the lauric acid is solid and 10 minutes has lapsed, removed the test tube from the beaker. Carefully remove the thermometer and reweight the test tube with the lauric acid. Record this mass.

Determination of Freezing Point of an Unknown Solution

- 1) Add 1 gram of the unknown acid into the test tube with solidified lauric acid.
- 2) Return the test tube and mixture to the hot water bath. Heat the solution until the mixture is liquefied, occasionally stirring the mixture with the thermometer ($60\text{-}80^\circ\text{C}$).
- 3) Once the mixture is a liquid, quickly move the test tube to the second beaker.
- 4) Repeat steps 5-8 from the first part of the experiment.
- 5) Add a second gram of the unknown organic acid and repeat the procedure for a second trial.
- 6) Reheat the solution until the thermometer can be removed. Pour the solution into the waste bottle. Rinse the test tube with acetone into the waste container. Also wash the thermometer with acetone into the waste container.
- 7) Wash out the test tube and thermometer in the sink.

Determination of the Validity of the van't Hoff Correction Factor

- 1) Calculate the freezing point depression that would result from 8.0 g magnesium chloride hexahydrate (molar mass = 203.31 g/mol) added to 10 mL of water.
- 2) Run the freezing point experiment for 8.0 g magnesium chloride hexahydrate in 10 mL at deionized water in a clean test tube and record the lowest temperature observed.
- 3) Calculate i , the van't Hoff correction factor, for magnesium chloride.

Data/Results

Mass of test tube = _____

Mass of lauric acid = _____

Mass of lauric acid (after freezing) + test tube = _____

Mass of unknown acid (trial #1) = _____

Mass of unknown acid (trial #1) + test tube (after freezing) = _____

Mass of unknown acid (trial #2) = _____

Mass of unknown acid (trial #2) + test tube (after freezing) = _____

Mass of magnesium chloride hexachloride = _____

Time	<i>Temperature (°C)</i>		
	Lauric Acid Only	Unknown Trial #1	Unknown Trial #2
0:00			
0:30			
1:00			
1:30			
2:00			
2:30			
3:00			
3:30			
4:00			
4:30			
5:00			
5:30			
6:00			
6:30			
7:00			
7:30			

8:00			
8:30			
9:00			
9:30			
10:00			

Lowest Temperature of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ($^{\circ}\text{C}$) = _____

Postlab Questions

- 1) Graph each trial with temperature on y-axis and time on x-axis. Do not connect the dots.
- 2) Using a ruler, draw a line back to the y-axis at the lowest temperature for each trial.
Record this as the freezing point.
- 3) Average the two freezing points of the unknown acid.
- 4) Calculate the molality of both lauric acid and the unknown acid based on the determined freezing point.
- 5) Calculate the moles of the unknown acid from the molality. Remember that lauric acid is the solvent.
- 6) Divide the mass of the unknown acid by the moles to determine the molar mass.
- 7) With the lowest temperature of magnesium chloride hexahydrate, calculate the van't Hoff correction factor (*i*).
- 8) A student fails to dissolve all the solute before measuring the freezing point of the solution.
 - (a) Will the freezing point of the solution be lower or higher than the freezing point observed if all the solute was dissolved? Explain.
 - (b) Will the calculated molar mass of the unknown acid be larger or smaller than one calculated from complete dissolution? Explain.
- 9) One mole of two different compounds happens to weigh the same, but one compound ionizes in water and one does not. Which will give the largest freezing point depression, ΔT_f ? Explain.
- 10) Explain why molality is used in lieu of molarity for colligative property measurements.

*Adapted from "Freezing Point Depression to Determine Molar Mass"—Bottomley, L;
Bottomley, L.A.; *Chem 1310: Laboratory Manual*, 2011-2012, p 133-140.